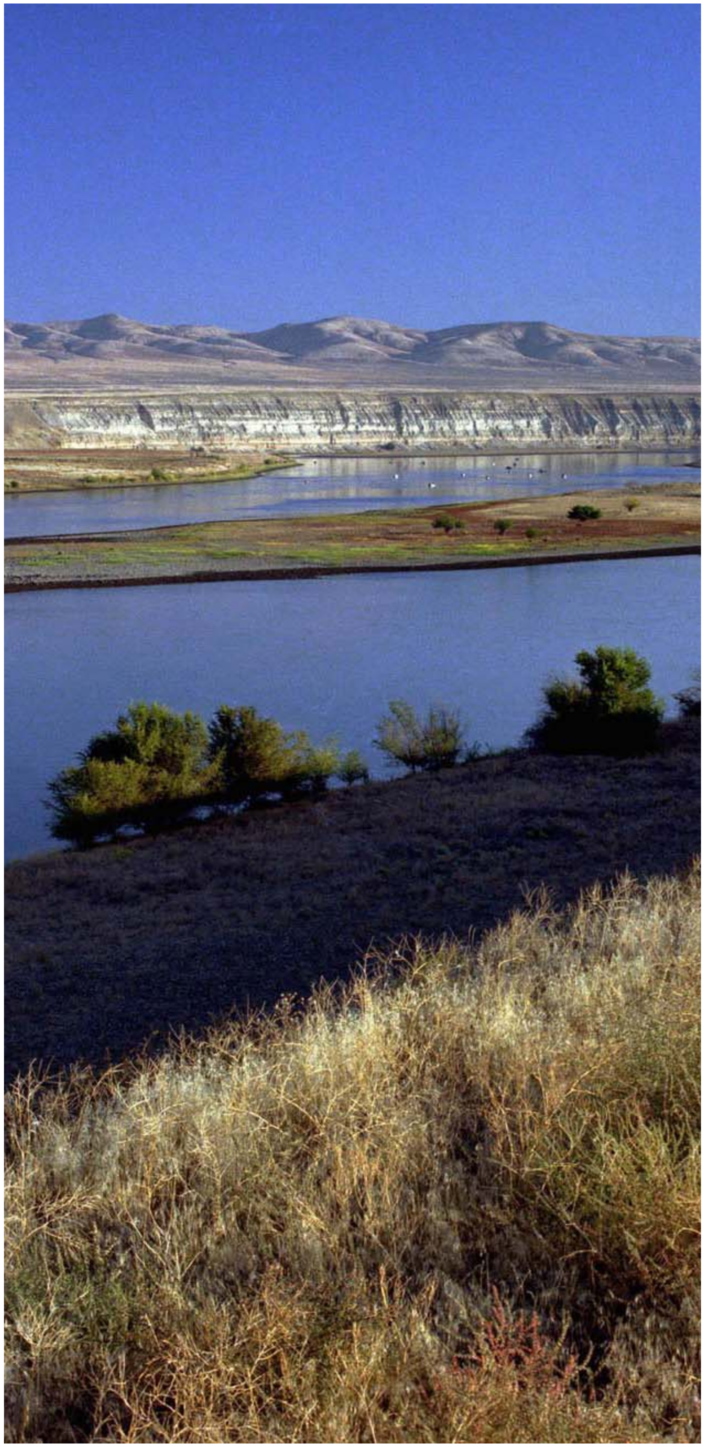

RPP-35256 Rev 0

Chemistry Optimization for Hanford Double-Shell Tanks

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Office of River Protection

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Overview

- Double-Shell Tank (DST) Waste Chemistry Controls Require Large Additions of Sodium Hydroxide to Maintain Required Chemistry Limits
- The Present DST Chemistry Limits are a “One Size Fits All” Specification from Seminal Corrosion Testing done at Savannah River (Ondrecjin) and followed up by work at PNNL (Devine), as described in the next slide.
- The Conservative Corrosion Controls were Reviewed by an Expert Panel Workshop and Considered Amenable to a Modern Accelerated Corrosion Testing Program, which was Initiated.
- The Results and Finding of this New Testing will be Described, along with the Enormous Benefits from Understanding the Role of DST Waste Constituents in Corrosion protection.

Basis for DST Chemistry Limits

- The majority of the requirements come from waste corrosion studies done by Ondrecjin (DP-1478) in the 1970's.
- His work examined the waste chemistry requirements for newly generated and concentrated waste at the SRS.
- In setting these requirements, SRS established a single set of requirements for operational simplicity.
- As such they established requirements for their worst case, which were not Post –Weld Heat Treated (PWHT), using A285 Carbon Steel exposed to temperatures up to 100 °C at pH > 11 in concentrated waste.

DST Waste Chemistry Limits*

FOR $[NO_3^-]$ RANGE	VARIABLE	FOR WASTE TEMPERATURE (T) RANGE		
		T < 167°F	167°F $\leq$ T $\leq$ 212°F	T > 212°F
$[NO_3^-] \leq 1.0M$	$[OH^-]$	$0.010M \leq [OH^-] \leq 8.0M$	$0.010M \leq [OH^-] \leq 5.0M$	$0.010M \leq [OH^-] \leq 4.0M$
	$[NO_2^-]$	$0.011M \leq [NO_2^-] \leq 5.5M$	$0.011M \leq [NO_2^-] \leq 5.5M$	$0.011M \leq [NO_2^-] \leq 5.5M$
	$[NO_3^-] / ([OH^-] + [NO_2^-])$	< 2.5	< 2.5	< 2.5
$1.0M < [NO_3^-] \leq 3.0M$	$[OH^-]$	$0.1 ([NO_3^-]) \leq [OH^-] < 10M$	$0.1 ([NO_3^-]) \leq [OH^-] < 10M$	$0.1 ([NO_3^-]) \leq [OH^-] < 4.0M$
	$[OH^-] + [NO_2^-]$	$\geq 0.4 ([NO_3^-])$	$\geq 0.4 ([NO_3^-])$	$\geq 0.4 ([NO_3^-])$
$[NO_3^-] > 3.0M$	$[OH^-]$	$0.3M \leq [OH^-] < 10M$	$0.3M \leq [OH^-] < 10M$	$0.3M \leq [OH^-] < 4.0M$
	$[OH^-] + [NO_2^-]$	$\geq 1.2M$	$\geq 1.2M$	$\geq 1.2M$
	$[NO_3^-]$	$\leq 5.5M$	$\leq 5.5M$	$\leq 5.5M$

* Except for AN-107 Interstitial Liquid

Sodium Additions to Hanford DSTs

- Sodium Hydroxide and occasionally Sodium Nitrite are added to the DSTs to maintain waste chemistry corrosion control
- From FY 2002 to FY 2007, 523.2 Metric Tons of Sodium were added to the Hanford DSTs
- At a projected WTP operating rate of ~ 3 MT/day, this amount alone represents over 174 days of WTP operation.
- Each 5,000 gal of 50% sodium hydroxide truckload adds 2.7 days to mission life

Sodium Additions to Hanford DSTs

- Single-Shell Tank waste retrievals to DSTs will continue to require hundreds of tons of NaOH additions.
- Similarly, large NaOH additions are required to periodically maintain the DSTs under the present waste chemistry limits, primarily from CO_2 depletion of the NaOH (Normally 20 - 40 KGal each time)
- Slow natural mixing of NaOH from the supernate to the sludge may require the installation of mixing pumps at ~$10M each, at present on 4 non-compliant DSTs

The Cost of Processing Sodium

- WTP capacity estimates range from 2 to 4.5 Metric Tons (MT) of sodium per day
- The Hanford RPP has an operating cost of about $600 million per year split between tank farm operations and WTP
- System Plan (Rev 2) states that the LAW capacity is 28.8 MT of Glass per day with a sodium oxide loading of 14%, which equates to three MT of sodium per day or 1100 MT of sodium per year
- Using the System Plan values each MT of sodium adds about $500,000 dollars to the life-cycle cost
- Each 1,000 gal of 50% sodium hydroxide increases mission cost by ~$1M

Expert Panel Workshops at Hanford

- PNNL-13571, Expert Panel Recommendations for Hanford Double-Shell Tank Life Extension, June 2001
  - Convened based on the need to ensure the integrity of DST past the 2028 operational horizon.
  - Reviewed programs at Savannah River and Hanford
  - Senior Review Committee developed and prioritized recommendations for life extension
- RPP-19438, Report of Expert Panel Workshop for Hanford Double-Shell Tank Waste Level Increase, January 2004
  - Provided basis for increasing waste level
  - Made recommendations for additional structural analysis to support further increases
- RPP-RPT-22162, Expert Panel Workshop for Hanford Site Double-Shell Tank Waste Chemistry Optimization, October 2004
  - Provided basis for tailoring sampling to chemistry changes in the tank sludges
  - Established program for changing tank chemistry
- RPP-RPT-31129, Expert Panel Workshop on Double-Shell Tank Vapor Space Corrosion Testing, October 2006
  - Reviewed instances of vapor space corrosion
  - Made recommendation to investigate potential for corrosion and testing methods for corrosion

DST Waste Chemistry Optimization Panel

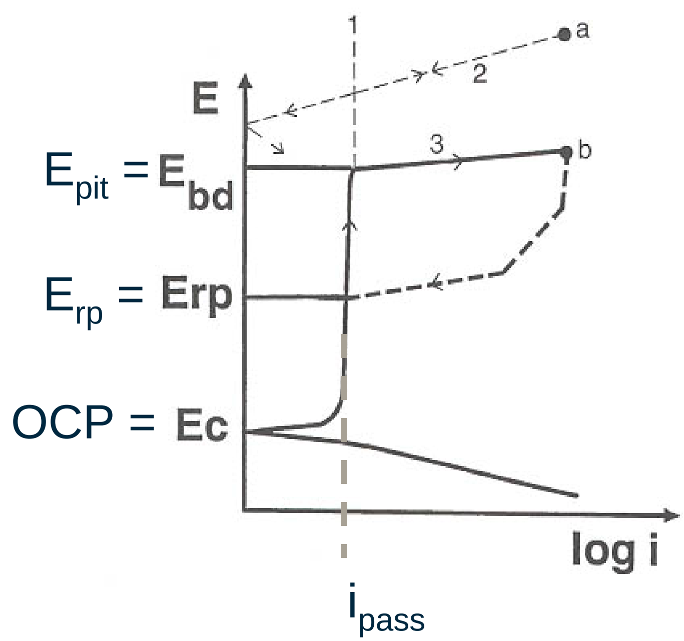
- Michael Terry, Chair, TFA Tank Safety, LANL (Retired)
- John Beavers, Research Director CC Technologies
- Gerald Frankel, Director Fontana Corrosion Center
- Bruce Wiersma, Fellow Engineer Tank Integrity Lead SRNL
- Leon Stock, Professor Emeritus University of Chicago

Accelerated Waste Chemistry Corrosion Testing

- Double-Shell Tank (DST) Accelerated Waste Corrosion Testing Consists of utilizing Multiple Techniques, as follows:
  - Waste simulant corrosion testing by Cyclic Potentiodynamic Polarization (CPP) measurements,
  - Slow Strain Rate (SSR) testing.
  - Crack Stress Intensity Factor (K1scc).

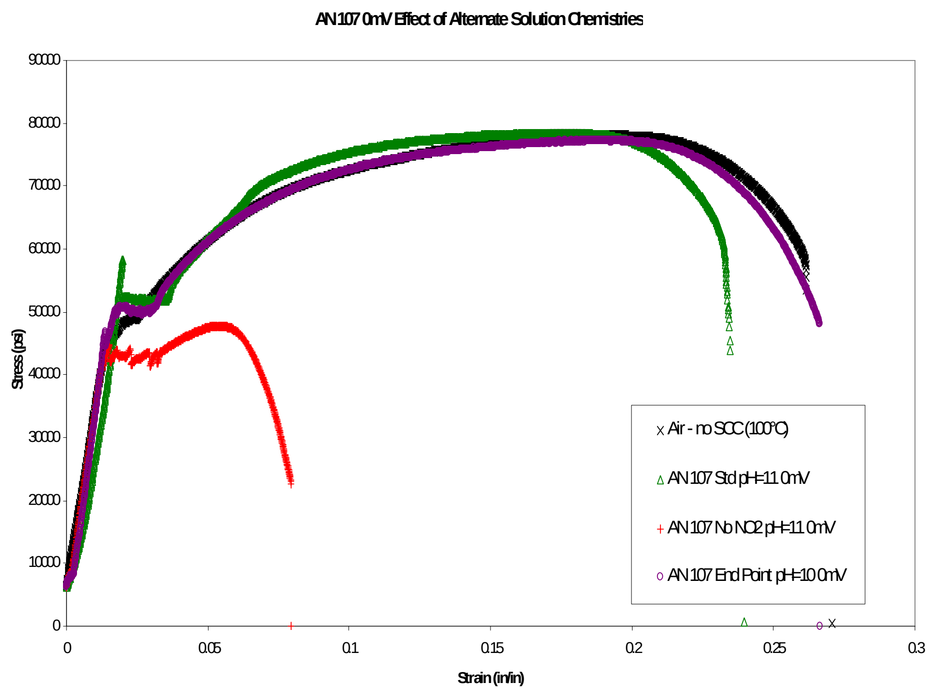
Overview of Approach

- Cyclic potentiodynamic polarization – determine overall electrochemical behavior of material in environments of interest
  - Key parameters: OCP, E_{pit}, E_{rp}, i_{pass}, pit depth/density, visual/metallographic examination



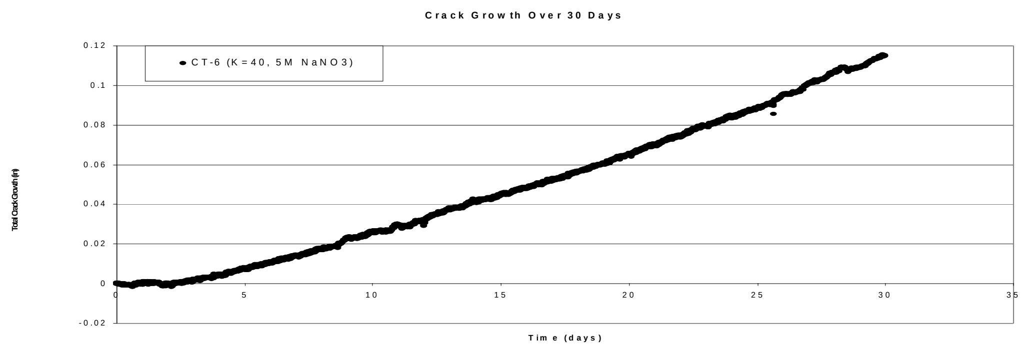
Overview of Approach

- Slow Strain Rate Testing
  - Key parameters: Time to failure, % strain to failure, estimated crack growth rate, visual or SEM metallographic examination

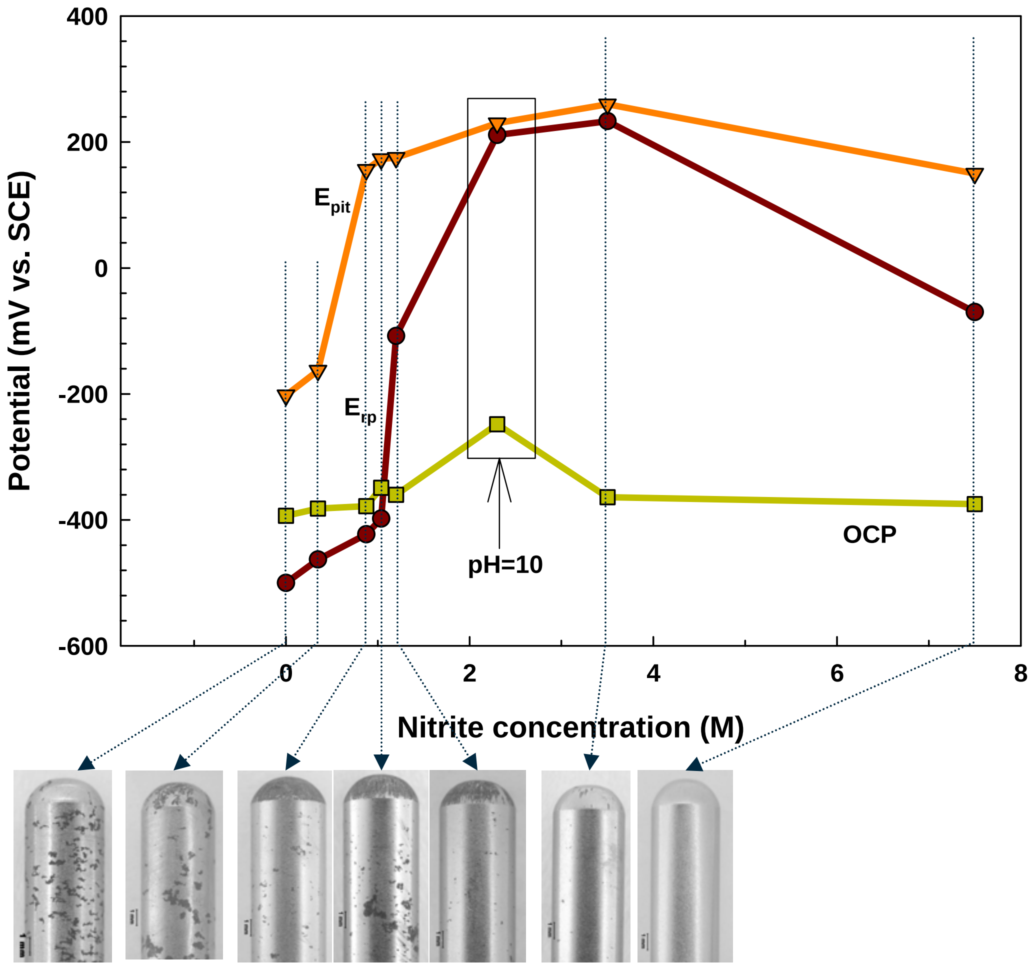


Overview of Approach

- Compact Tension Crack Growth Rate Tests
  - Key Parameters: crack growth rate

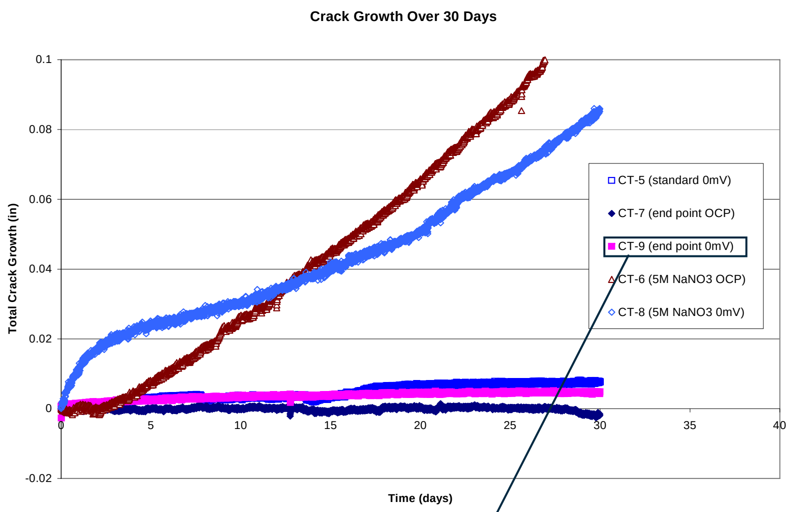


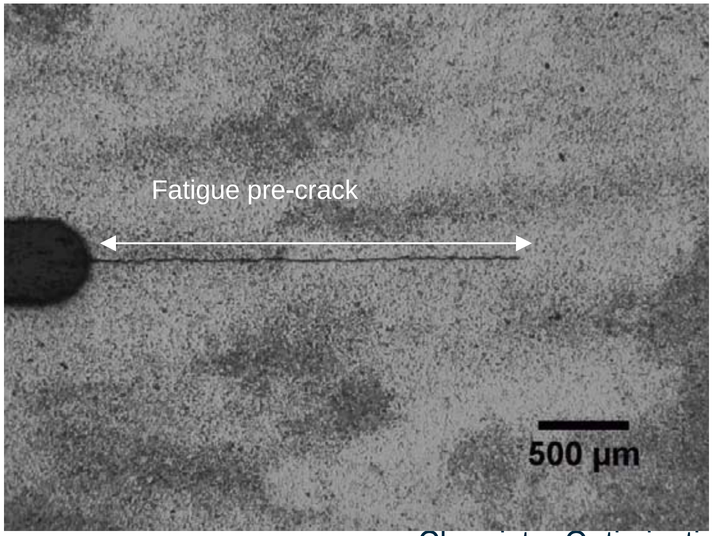
Summary of Results – Effect of NO_2 on Pitting Behavior



- E_{pit} and E_{rp} strong functions of NO_2^- concentration
- OCP nominally independent of NO_2^-
- NO_2^- acts as pitting inhibitor

Summary of Results – Effect of NO_2^- on Crack Growth

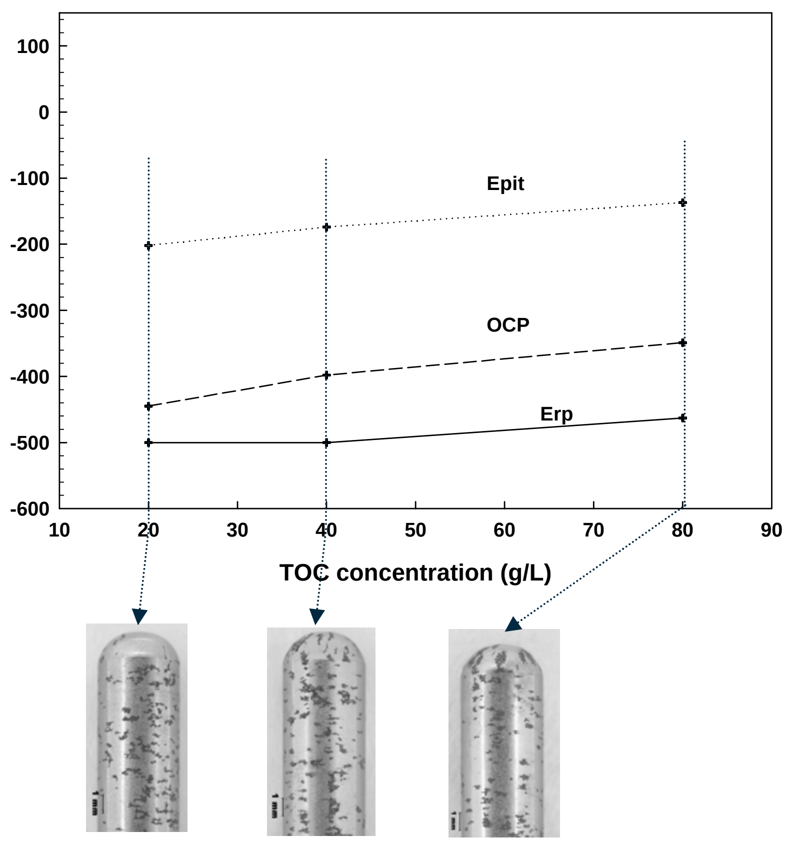




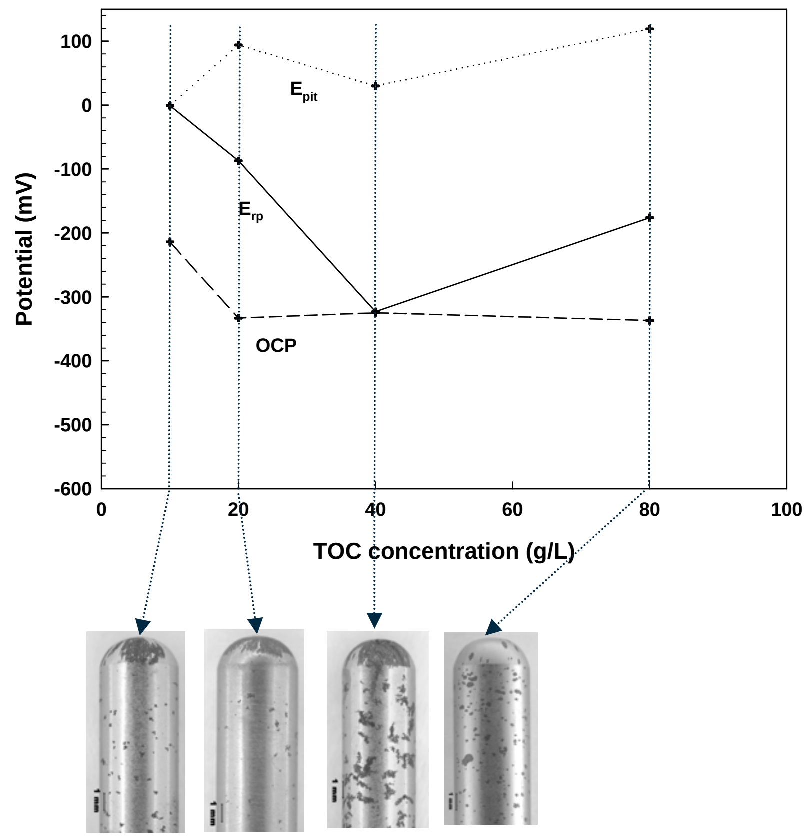
- NO_2^- inhibits crack growth

Summary of Results – Effect of TOC

pH 11, no NO_2^-

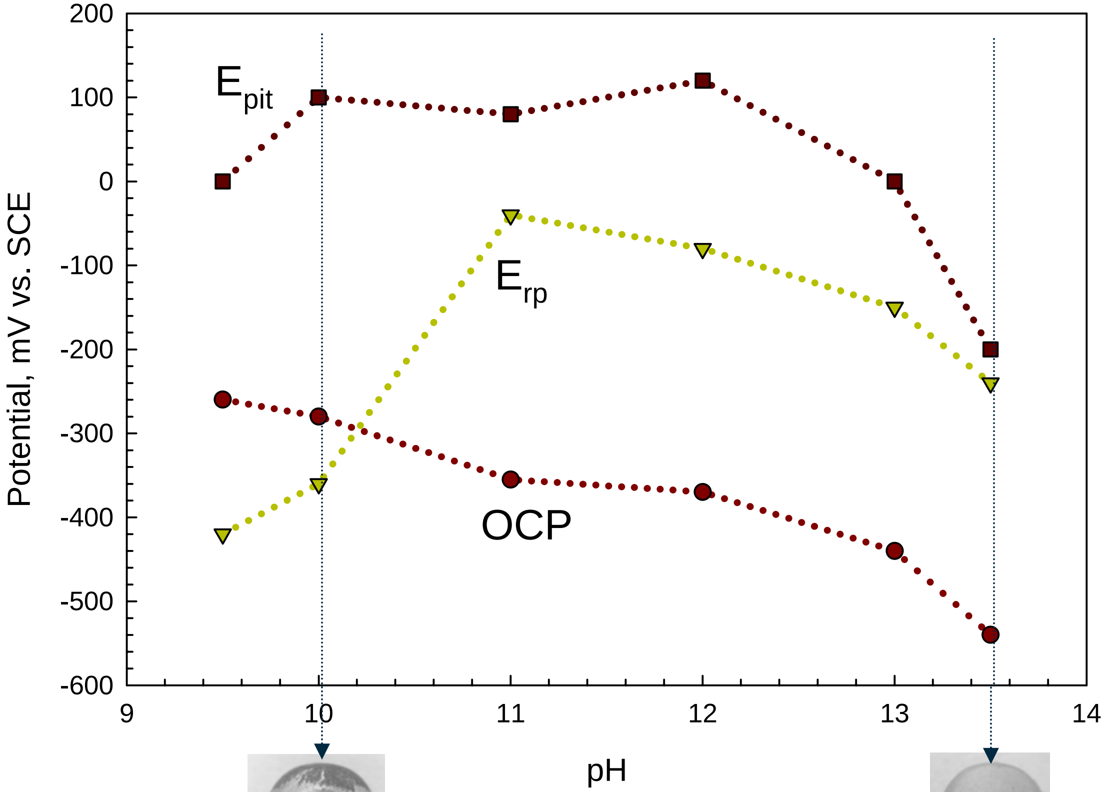


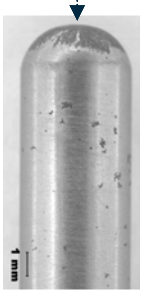
pH 11, 1.2M NO_2^-



- TOC appears to be weak pitting inhibitor
- May also be detrimental under some conditions

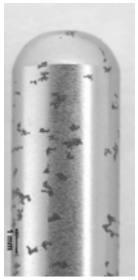
Summary of Results – Effect of pH





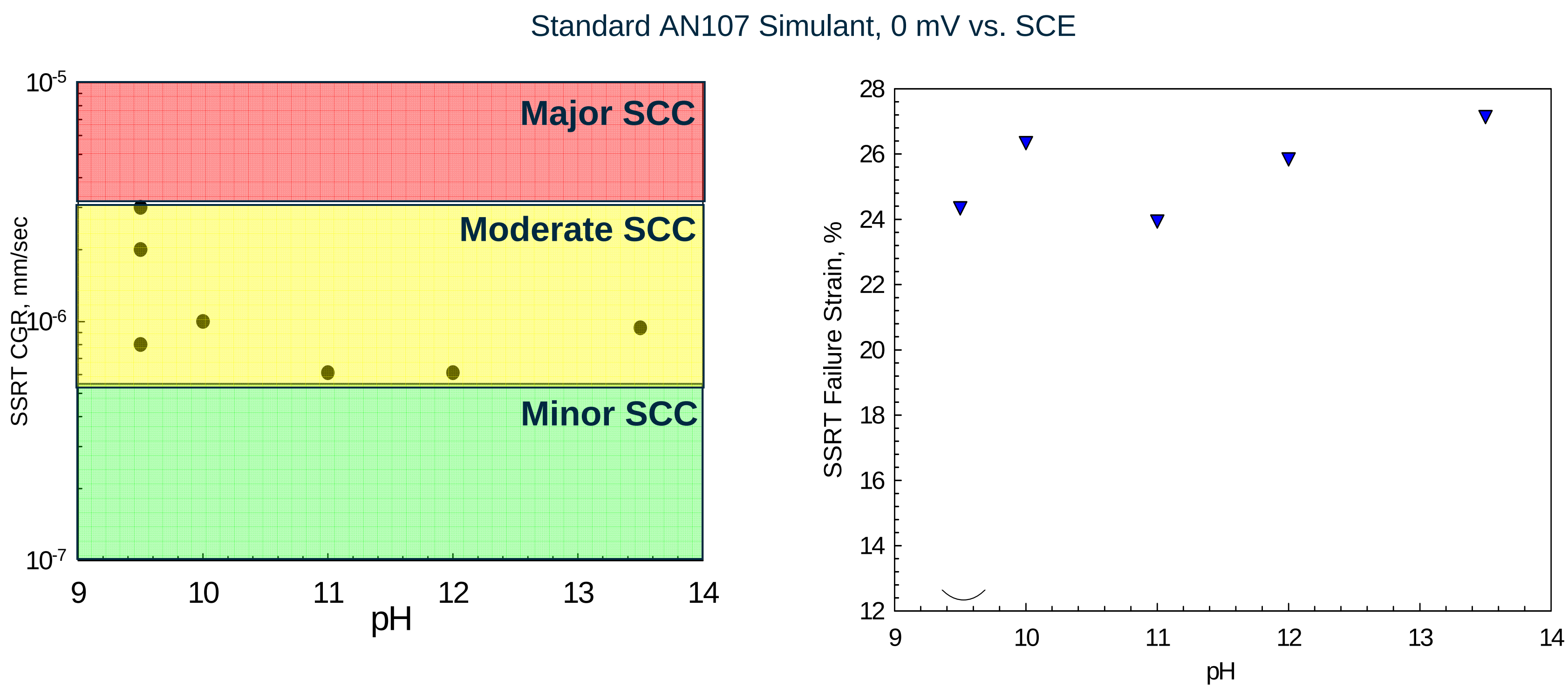
- Higher pH generally inhibits pitting

  (higher E_{rp}, smaller [E_{pit} – E_{rp}])



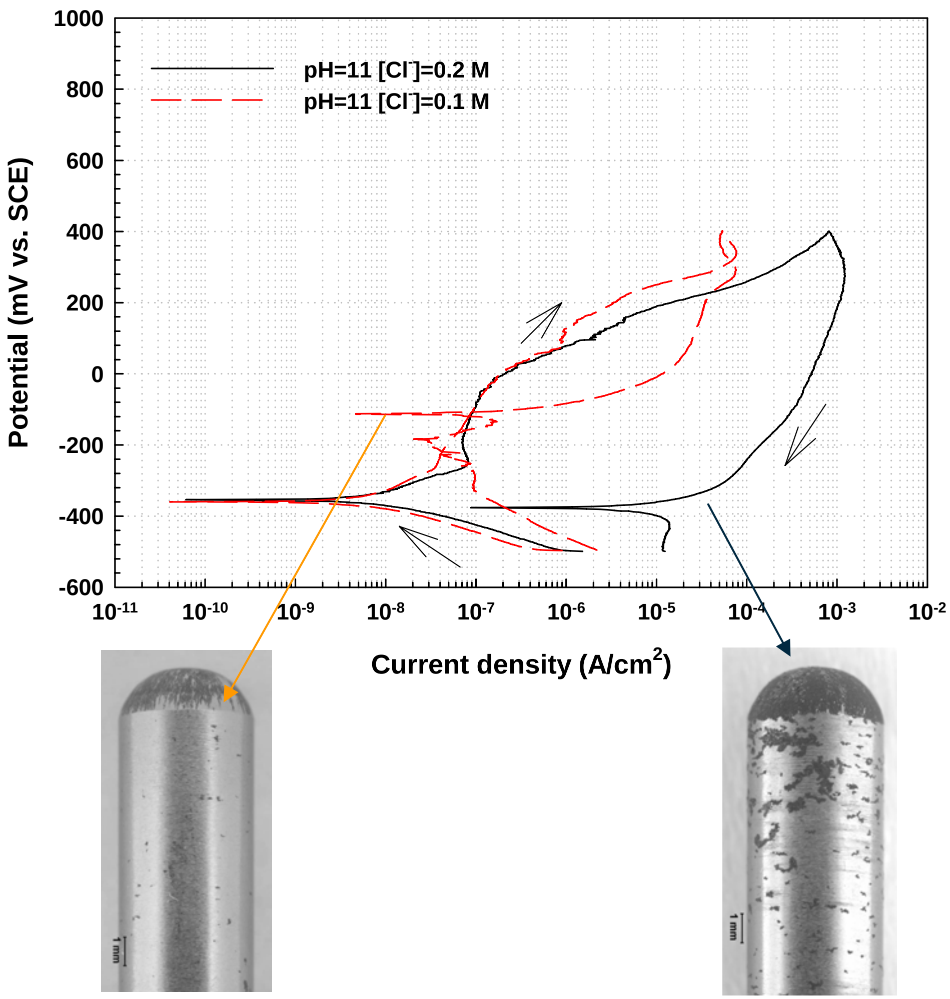
w/o NO_2^-
(high pH cannot overcome lack of NO_2^-)

Summary of Results – Effect of pH



- SCC results independent of pH (for standard AN107 simulant at 0 mV vs. SCE)

Summary of Results – Effect of Cl^-

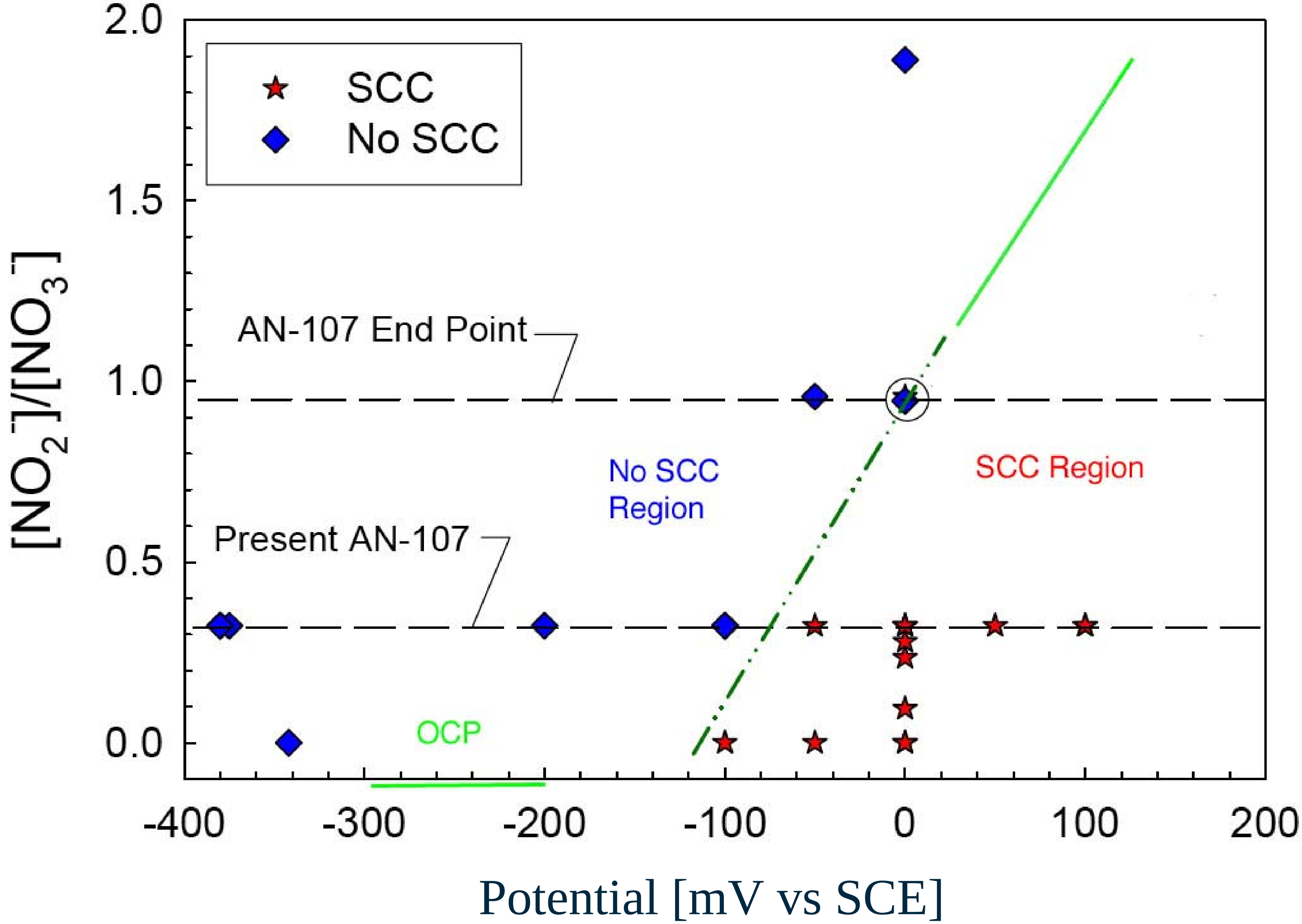


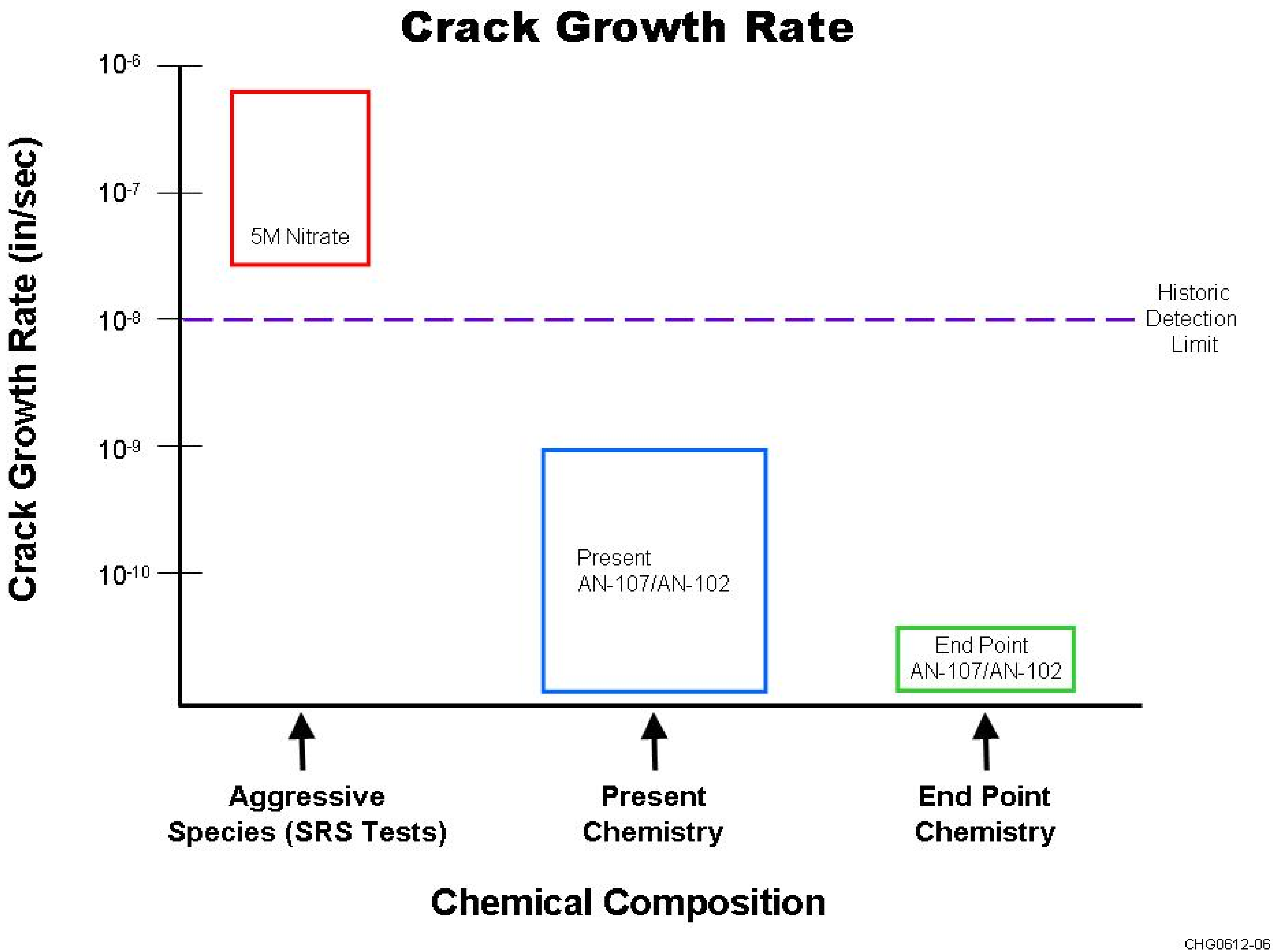
- OCP - no change
- E_{pit} – no change (surprising)
- E_{rp} - suppressed significantly by higher Cl^-
- Nitrite effectively offsets Cl^- effects

Summary of Findings

- Nitrite – strong inhibitor for pitting and SCC
- TOC – weak inhibitor; sometimes detrimental
- pH – weak inhibitor
- Potential – appears to be a threshold for cracking (environment dependent)
- Chloride – affects pitting behavior
- Crack Intensity Factor for SCC (K_{1SCC}) appears to be ~ 20 – 30 ksi√in at 0 mV SCE

Nitrite Effect on SCC




Crack Growth Rate
Crack Growth Rate (in/sec)
10-6
10-7
10-8
10-9
10-10
5M Nitrate
Historic Detection Limit
Present AN-107/AN-102
End Point AN-107/AN-102
Aggressive Species (SRS Tests)
Present Chemistry
End Point Chemistry
Chemical Composition
CHG0612-06

Vapor Space & Supernate Chemistry

- Supernate chemistry requirements will not change until Vapor Space Corrosion is Studied (underway)
  - Vapor space corrosion will not be different than any other DST under current limits (i.e., supernate is within present requirements)
  - Specification will only change for interstitial liquid in the sludge
  - An operating EN probe was in place for 4 years in AN-107, and showed very low corrosion activity in the vapor space, supernate and sludge
- Prior to changing supernate waste chemistry limits in any DST
  - Will establish knowledge of importance/significance of waste chemistry factors and other parameters (e.g., ventilation) on VSC, before moving forward
- Changing supernate chemistry will avoid the addition of ~325 MT of sodium, and free up that DST volume for waste retrievals

New Optimized Chemistry Controls - Nitrite Based

- No increase in DST Risk
  - Current chemistry controls are based on limited testing data and require controls to be conservatively bounding.
  - New testing data provides in depth understanding of material performance and allows for the selection of more appropriate bounding controls.
  - Expert Panel Decision Process selects controls which are shown to maintain tank protection.
  - Will ensure the vapor space region will not be adversely affected by changes in supernate chemistry before any changes are authorized.
  - Consequences of a tank leak do not change, and DST life extension justified.
- Increase in Benefits
  - Plan to expand optimized chemistry controls to all other DSTs and supernatant layers using the established decision process (presently looking at carbonate dominated waste).
  - Massive reduction in volume of sodium hydroxide added to DSTs
  - Eliminate operator risks, exposure and costs associated with mixer pump installation or caustic additions
  - Reduced Sodium content in waste will allow increased waste loading in WTP glass and reduced WTP processing time.